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Parallel synthesis of alkyl methacrylate latexes for use as catalytic media

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Among thirty-two anion exchange latexes prepared by parallel synthesis, those containing 2-ethylhexyl methacrylate units are the most active as catalytic media for alkaline hydrolysis of *p*-nitrophenyl alkanecarboxylates.

Cationic polymers and colloids, such as soluble polyelectrolytes,¹ macroscopic anion exchange resins,² surfactant micelles,^{1,3} and 0.2 µm diameter latex particles⁴ in aqueous media catalyze reactions of anions with uncharged organic compounds. The catalytic activities are due primarily to high local concentrations of the anionic and uncharged reactants in the small volume fraction of the polymer or colloid phase or pseudophase in the aqueous mixture, although enhanced intrinsic rate constants sometimes contribute. Amounts of less than 1 mg ml⁻¹ of polystyrene latexes containing quaternary ammonium anion exchange sites increase the rate of *o*-iodosobenzoate-catalyzed hydrolysis of *p*-nitrophenyl diphenyl phosphate up to 6300 times faster than in water alone.⁴ These rate enhancements in anion exchange latexes are as high or higher than those in cationic micelles,⁵ and the activity persists at very low particle concentrations, whereas surfactants have high catalytic activity only above the critical micelle concentration.

An important potential application of colloidal catalysts is hydrolytic decontamination of toxic organophosphates, phosphonates and fluorophosphonates which are widely used as insecticides and are stockpiled as chemical warfare agents.⁶ However, these polystyrene latex particles failed to promote the hydrolysis of diisopropyl fluorophosphate (DFP) in pH 11 aqueous media,⁷ probably due to an unfavorable partition coefficient of the aliphatic DFP into the aromatic polystyrene latex particles. Reasoning that aliphatic polymers would absorb larger amounts of aliphatic reactants, we synthesized a family of cationic latexes from copolymers of alkyl methacrylates and vinylbenzyl chloride and tested their activities for basic hydrolysis of active esters.

Diversity strategies for the synthesis of biologically active compounds are employed at all major pharmaceutical companies, have been used in search of superconductive, magnetic, and phosphorescent materials,⁸ and have been used to prepare polymer catalysts.⁹ One widespread method is the combinatorial synthesis of different compounds in polymer beads that can be separated and tested individually. Since latex particles are too small to be separated as single beads, we employed a parallel method to prepare a diverse series of alkyl methacrylate-based catalysts.

Twenty-nine latex copolymers of 25 mass% vinylbenzyl chloride (VBC, 70:30 *m:p*) and 73 mass% aliphatic methacrylates were prepared on a 500 mg scale using 1% divinylbenzene to cross-link the particles, 1% (*m,p*-vinylbenzyl)-trimethylammonium chloride to stabilize the particles during growth, and 2,2'-azobis(*N,N'*-dimethyleneisobutyramidine) dihydrochloride as a water-soluble radical initiator. The latexes differed in the number and combination of aliphatic monomers present. Polymerizations were carried out using sets of 12 test tubes, each containing a different mixture of monomers and a 7 mm stirring bar. The test tubes were supported in a 60 °C water bath on a multiplate magnetic stirrer. Anion exchange sites in the form of quaternary ammonium groups were introduced to

six latexes at one time in separate vials in a sealed pressure reactor by reaction of the vinylbenzyl chloride component with either trimethylamine (TMA) at 60 °C or tributylamine (TBA) at 95 °C. Methanol was added to the vials and to the reactor to promote permeation of the polymers by the amines and to equalize pressure inside and outside the vials. Each quaternized latex was purified by repeated washing and ultrafiltration through a 0.1 µm membrane filter on a syringe. The resulting anion exchange particles contained 19–20 mol% of quaternary ammonium units (Fig. 1). Representative samples were 130–140 nm in diameter by TEM measurements.

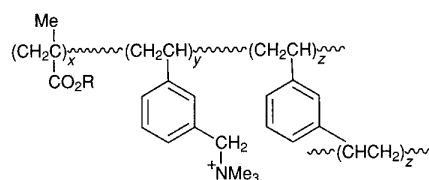


Fig. 1 Structure of TMA-quaternized latexes

Table 1 presents the results of screening the catalytic activities of 0.6 mg ml⁻¹ alkyl methacrylate latexes for hydrolysis of *p*-nitrophenyl (PNP) hexanoate (Scheme 1) in pH 9.4 borate buffer solution.

Rate enhancements relative to rates in the absence of latex ranged from 2.3 for the polystyrene–TMA latex (15 in Table 1)

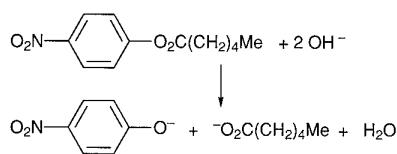
Table 1 Observed rate constants for hydrolysis of PNP–hexanoate in latex dispersions

Latex	Methacrylate ^{a,b}	10 ³ <i>k</i> _{obs} /s ⁻¹
1	Butyl	2.0
2	Isobutyl	2.1
3	2-Chloroethyl	1.8
4	Tetrahydrofurfuryl	2.3
5	2-Ethylhexyl	4.1
6	Butoxyethoxyethyl	1.9
7	Ethoxyethoxyethyl	1.8
8	2-Ethylbutyl	2.0
9	<i>n</i> -Hexyl	2.1
10	<i>n</i> -Octyl	3.1
11	<i>n</i> -Decyl	3.3
12	<i>n</i> -Dodecyl	3.5
13	Tetrahydropyranlyl	1.8
14	Furfuryl	1.9
15	Polystyrene	0.8
16	Butyl (TBA)	5.1
17	Polystyrene (TBA)	3.9
18	2-Ethylhexyl (TBA)	5.4

^a All latexes were quaternized with trimethylamine except 16, 17 and 18 which were quaternized with tributylamine. ^b Latex concentration was 0.6 mg ml⁻¹, quaternary ammonium ion concentration [N⁺] = 62 µM, and substrate concentration 2.5 µM in 0.02 M borate buffer (pH 9.4) at 30.0 °C. Pseudo-first-order rate constants were calculated for formation of *p*-nitrophenoxide measured by increase of absorbance at 410 nm over the first 20% conversion. The *k*_{obs} values were reproducible to within 5% from triplicate measurements with each latex, and from triplicate preparations of latexes 1, 5 and 15–18. *k*_w for the reaction in the absence of latex was 3.26 × 10⁻⁴ s⁻¹.

Table 2 Intraparticle rate constants and equilibrium constants

PNP ester	Styrene		Butyl MA		2-Ethylhexyl MA	
	$10^3 k_t/s^{-1}$	$10^{-3} K/dm^3 mol^{-1}$	$10^3 k_t/s^{-1}$	$10^{-3} K/dm^3 mol^{-1}$	$10^3 k_t/s^{-1}$	$10^{-3} K/dm^3 mol^{-1}$
TMA-quaternized						
Acetate	1.3	2.0	9.3	2.3	7.4	2.3
Hexanoate	5.7	2.1	5.9	11.8	4.7	21
Octanoate	4.7	12.7	5.3	46	4.9	70
TBA-quaternized						
Acetate	11.9	3.1	9.5	4.1	9.0	5.0
Hexanoate	5.8	15.1	5.8	25	5.8	31
Octanoate	5.7	69	5.3	74	5.1	88



Scheme 1

to 16.5 for the 2-ethylhexyl methacrylate-TBA latex (18), and all alkyl methacrylate-TMA latexes were more active than the polystyrene-TMA latex. There was a sizable increase of activity on increase of the alkyl chain length from hexyl (9) to octyl (10) but only smaller increases between other pairs of C_{2n} -alkyl methacrylate latexes (1, 9–12). The branched 2-ethylhexyl methacrylate latex (5) was more active than the linear octyl methacrylate latex (10) having the same number of carbon atoms. Fourteen more TMA-quaternized latexes (not shown) containing mixtures of two methacrylate monomers and VBC gave rate constants between those of the latexes in Table 1 containing the same individual monomers. Finally Table 1 indicates that particles containing TBA sites (16–18) are more active than those containing TMA sites (1,5,15).

Activities of the styrene, butyl methacrylate and 2-ethylhexyl methacrylate-based latexes were measured at 5–6 different particle concentrations. Pseudo-first order intraparticle rate constants (k_t) for the hydrolysis of PNP-acetate, hexanoate, and octanoate and equilibrium binding constants (K) of the PNP ester to quaternary ammonium ion sites in the latex were calculated from double reciprocal plots of duplicate measurements of each rate constant using eqn. (1), where k_w is the rate

$$1/(k_{obs}-k_w)=1/(k_t-k_w)K[N^+]+1/(k_t-k_w) \quad (1)$$

constant in the absence of latex.¹⁰ (A 'binding constant' of the nonionic PNP ester to the ion exchange sites is a misnomer. 'Partition coefficient' would be better, but the binding constant formalism¹⁰ is easy to apply.) The results are reported in Table 2.

The major differences in the activities are due to the binding constants: the longer the aliphatic chain of the PNP ester, and the more lipophilic the quaternary ammonium ion, the greater

the binding constant. The much larger increases in the binding constants from polystyrene-TMA to polystyrene-TBA than with the corresponding methacrylate latexes is due to the TBA increasing the aliphatic character of aromatic latexes more than of aliphatic latexes.

Parallel synthesis has enabled rapid evaluation of 32 latex catalysts and selection of the most informative ones for analysis of intraparticle rate constants and binding constants. This diversity approach can be used to identify active polymer catalysts for many other important chemical reactions.

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Notes and References

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